

2. The objects of investigation: substrate and adsorbates

2.1. The substrate: gold (110)-(1×2)

THE ELEMENT GOLD is a very noble metal ($\epsilon^0(\text{Au}/\text{Au}^{3+}) = +1.498 \text{ V}$) and belongs to the nine elements¹ which occur in the nature in a pure, native state. For this reason, gold was known and, because of its beauty and rareness, highly valued from earliest times. Egyptian inscriptions dating back to 2600 B.C. describe gold, it is mentioned several times in the Old Testament, and it is one of the elements which have an alchemical symbol: \odot . Its English (and German) name is assumed to originate from the Old English word *geolo* (yellow), while the chemical symbol, Au, is derived from the Latin word *aurum*. Pure gold crystallizes in a face-centered cubic lattice (space group Fm-3m) with a lattice constant of 4.0782 Å. A selection of further data is presented in Table 2.1.

THE CLEAN Au(110) SURFACE reconstructs and shows a 1×2 LEED superstructure. A similar reconstruction was observed on Pt(110) and Ir(110). From a comparison of experimental and calculated LEED-I(V) curves of the Au(110) surface Moritz et al. [Mo79] inferred a missing-row reconstruction as displayed in Fig. 2.1.

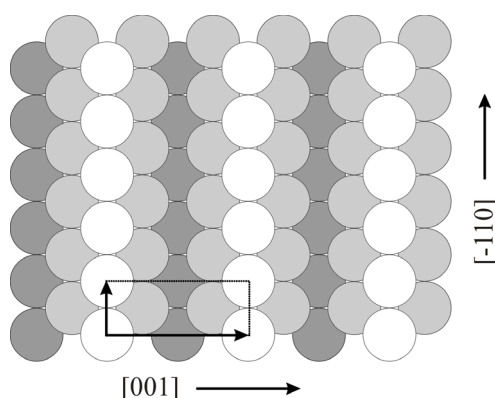


Fig. 2.1: Model of the missing-row reconstructed Au(110)-(1×2) surface with unit cell.

Compared to the unreconstructed surface, every second row of atoms parallel to the $[\bar{1}10]$ direction is missing in the first layer. This leads to the formation of trenches with (111) microfacets on both sides. The surface unit cell with the dimensions $2.89 \text{ Å} \times 8.16 \text{ Å}$ contains four atoms, one in the first, two in the second, and one in the third layer. The distance between first and second layer, and thereby, the depth of the trenches, is significantly reduced due to relaxation.

¹ The other elements are: Cu, Ag, Pt, Fe (l), As, Bi, S, C.

Property	Value	Ref.
atomic weight	196.96655 (2)	[www1]
melting point [K]	1337.33	[www1]
boiling point [K]	3129	[www1]
natural isotopes and nuclear spin	$^{197}_{79}\text{Au}$ (100%) 3/2 (NMR!)	[www1]
atomic radius [Å]	1.442 (in the element) 1.35 (in compounds)	[www1]
van der Waals radius [Å]	1.66	[www1]
ionic radii [Å]	0.71 (+5, c.n.= 6, octahedr.) 0.82 (+3, c.n.= 4, square-planar) 0.99 (+3, c.n.= 6, octahedr.) 1.51 (+1, c.n.= 6, octahedr.)	[www1]
work function [eV]	5.1 (Au_{poly}), 5.47 ($\text{Au}(100)$) 5.37 ($\text{Au}(110)$), 5.31 ($\text{Au}(111)$)	[Hü96]
electronegativity	2.54 (Pauling ²) 1.42 (Allred and Rochow ³) 1.87 (Mulliken ⁴)	[Al61] [www1] [www1]
hardness ⁵ [eV]	5.6 (Au^+) 8.4 (Au^{3+})	[Pe88]

Table 2.1: Physical and chemical properties of gold.

The driving force for the reconstruction is the minimization of the surface energy. Garofalo et al. [Ga87] calculated the surface energy for several structural models. They found that a distorted (1×2)-missing-row structure is only slightly favoured compared to the 1×3 and 1×4 missing-row reconstructions. This result was a theoretical confirmation of earlier STM investigations by Binnig et al. [Bi83], who found mainly 1×2 domains, but also 1×3 and 1×4 reconstructed areas. Further theoretical studies also show that only a sufficient density of binding d-electrons is able to stabilize the reconstructed modification of the surface. This is the reason why gold (110) reconstructs, in contrast to clean silver (110). However, reconstruction of the silver surface is induced by low coverages of alkali

² Electronegativity difference $x_A - x_B$ given by $D_{(A-B)} = [D_{(A-A)} D_{(B-B)}]^{1/2} + 30(x_A - x_B)^2$ with the experimental bond energies D [Al61, Pa60].

³ Allred-Rochow electronegativity $\chi_{AR} = 0.744 + 0.395 Z_{\text{eff}}/r$ with the covalent radius r and the effective nucleus charge Z_{eff} [Al58].

⁴ Mulliken electronegativity $\chi_M = (IP + EA)/2$ with the ionization potential IP and the electron affinity EA [Br88, Mu34, Mu35].

⁵ Hardness $\eta = (IP - EA)/2$ (after Pearson [Pe63, Pe68, Pa83, Pe88, Pe93]).

metals, which act as electron donators and enhance the electron density in the surface region. Reversely, electron acceptors like NO or CO reduce the local electron density and, thereby, lift the reconstruction e.g. of Pt(110)-(1×2) [Mo69, Bo73, Co76, He76]. Up to now, including the present study, this effect has only been observed on Pt and Ir [Ch73a, Ni78], but not on gold, which is the electron-richest of the three [He86, Fo87, Ga87, Ho87, Ho87a, Gu89, Le98, this work].

The Au(110)-(1×2) surface shows an order-disorder transition with critical temperatures, T_c , between 650 K and 695 K depending on finite-size effects [Cl86]. SPA-LEED experiments suggest that the thermal roughening of this surface, which is not fully reversible, starts already below T_c [Ro91].

THE CHEMISTRY OF GOLD is largely dominated by a relativistic orbital contraction, which occurs similarly pronounced only in the case of mercury. The s orbitals (and, to a lesser extent, also the p orbitals) are energetically lowered and spatially contracted, the d and f orbitals are energetically raised and expanded. The electron configuration of gold is $[\text{Xe}]4f^{14}5d^{10}6s^1$. The 5d level is higher, the 6s level lower than a comparison with the congener Ag suggests. This relativistic effect leads to the following remarkable properties of gold [Ba98]:

(a) The reduced 6s-5d separation of ≈ 2 eV (as compared to ≈ 3.5 eV for the 5s-4d separation in the silver atom) allows an optical transition in the visible range (adsorption for $\lambda < 560$ nm), which causes the yellow colour of bulk gold.

(b) The energetically lowered 6s orbital is only half occupied, which explains why both the first ionization potential, IP, and the electron affinity, EA, are higher as in the case of Ag (Table 2.2). The EA of Au is the highest of all metals and ranges between the values for oxygen (1.465 eV) and iodine (3.063 eV). This may explain why Au shares several properties with the halogens, while Hg, the following element in the periodic system, behaves partly like a closed-shell element. Gold vapour consists of remarkably stable molecules Au_2 with a dissociation energy of 232 kJ/mol (cf. Cl_2 : 244 kJ/mol) [Ho85]. It is clear from Mulliken's definition of the electronegativity, χ_M , as the average of IP and EA that high values of IP and EA also lead to a high electronegativity. Thus, gold has the highest (Pauling) electronegativity of all metals (see Table 2.1). This manifests itself, e.g., in the existence of the aurid Cs^+Au^- , which is a non-metallic semiconductor.

[eV]	Ag	Au
1 st ionization potential	7.576	9.225
2 nd ionization potential	21.49	20.5
electron affinity	1.202	2.039

Table 2.2: Ionization potentials and electron affinities of silver and gold (after [Ba98]).

(c) The destabilization of the d levels explains the existence of high oxidation states of Au as, e.g., +3 (AuCl₃), +5 (AuF₅), and even +7 (AuF₇). The most stable oxidation state is +3, in contrast to +1 in the case of silver.

2.2. The adsorptives

In this work, we studied the adsorption of oxygen, carbon monoxide, carbon dioxide, and ethylene on a gold (110)-(1×2) surface.

2.2.1. Oxygen

THE ELEMENT – The oxygen molecule (symmetry D_{∞h}) possesses, due to its ground state electron configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$, a triplet ground state, $^3\Sigma_g^-$, and a MO binding order of 2. The lowest excited states of the molecules are the singlet states $^1\Delta_g$ (+0.96 eV) and $^1\Sigma_g^+$, in which the $1\pi_g^*$ electrons have antiparallel spin and occupy the same ($^1\Delta_g$) or different ($^1\Sigma_g^+$) $1\pi_g^*$ orbitals.

Dioxygen condenses at 90.2 K forming a pale blue liquid. Thus, the boiling point is higher than that of the neighbours in the periodic system, N₂ (77.35 K) and F₂ (85.1 K), which is a result of the intermolecular interactions in the liquid, mediated by the unpaired electrons. At 54.4 K, liquid O₂ solidifies to cubic γ -O₂, which undergoes transitions to trigonal β -O₂ at 43.8 K and to monoclinic α -O₂ at 23.9 K [K194]. The O₂ molecule has a bond length of 1.20741 Å and a dissociation energy of 498.67 kJ/mol [www1]. Further properties of the oxygen atom are collected in Table 2.3.

The bended ozone molecule (O₃, symmetry C_{2v}) is another, metastable allotrope of oxygen. It is formed under the influence of electrical discharges or ultraviolet light on O₂ and possesses a singlet ground state. The O-O bond length is 1.278 Å, the bond angle 116.8°. The decomposition of O₃ is strongly exothermic (157 kJ/mol). Under standard pressure, ozone melts at 80.6 K and boils at 162.65 K [K194]. Ozone has been used to produce chemisorbed oxygen on gold surfaces [Pa90, Ki95, Kr97, Sa98].

INTERACTION OF OXYGEN WITH BULK GOLD – A noble metal, gold has a low affinity towards oxygen. Accordingly, only a small number of gold-oxygen compounds exists [Gm92, Ja99], while the two other coinage metals, silver and copper, possess a considerable oxide chemistry. The only well-characterized among the metastable oxides is the Au₂O₃, which possesses a very large unit cell containing a complicated network structure of corner-linked distorted square-planar [AuO₄]-units (space group Fdd2) [Jo79]. For the standard enthalpy of formation, $\Delta_f H_{298}^0$, values between –13 [As72] and +81 kJ/mol have been reported, for the standard Gibbs enthalpy of formation, $\Delta_f G_{298}^0$, +77 and +163.2 kJ/mol (see [Gm92] for references). The

thermogravimetric analysis of Au_2O_3 revealed two subsequent processes. The first, exothermic, process started at 402 K and reached its maximum at 449 K. This reaction was regarded as a polymorphic phase transition, since no mass loss was detected. The second, endothermic, reaction started at 581 K, reached a maximum at 633 K, and the mass loss was the one expected for the reaction $\text{Au}_2\text{O}_3(\text{s}) \rightarrow 2\text{Au}(\text{s}) + (3/2)\text{O}_2(\text{g})$ [As72].

Property	Value	Ref.
atomic weight	15.9994 (3)	[www1]
natural isotopes, relative abundance, and nuclear spin	$^{16}_8\text{O}$ (99.757 %) (0) $^{17}_8\text{O}$ (0.038 %) (5/2) $^{18}_8\text{O}$ (0.205 %) (0)	[www1]
1st ionisation potential [eV]	13.618	[www1]
2nd ionisation potential [eV]	35.117	[www1]
electron affinity [eV]	1.465	[Ho85]
van der Waals radius [Å]	1.52	[www1]
atomic radius [Å]	0.60	[www1]
covalent radius [Å]	0.73 (single bond)	[www1]
ionic radius [Å]	1.38 (O^{2-} , c.n.= 4)	[Pe89]
electronegativity	3.44 (Pauling [Al61, Pa60]) 3.50 (Allred and Rochow [Al58]) 3.41 (Mulliken [Br88, Mu34, Mu35])	[www1]
hardness [eV]	6.08	[Pe88]

Table 2.3: Physical and chemical data of the oxygen atom.

There is no reliable evidence for the existence of Au_2O , although a number of claims were made for the preparation of this oxide. The same holds for *solid* AuO . *Molecular* AuO , which exists in the gas phase [He80] can be stabilised in an inert gas matrix [Gr77]. A relativistic calculation of the AuO molecule, taking into account the electron correlation, provided the following parameters for the Au-O bond: $r_e = 1.946 \text{ \AA}$, $D_e = 146.6 \text{ kJ/mol}$, $\mu_e = 3.41 \text{ D}$ [Sc89]. Another value for the Au-O binding energy that has been published is $221.8 \pm 20.9 \text{ kJ/mol}$ [CRC94]. A complex compound with O_2 , the dioxygen-gold $\text{Au}(\text{O}_2)$, which is characterized by a side-on Au-O_2 bond, was obtained by means of co-condensation of monoatomic Au with O_2 [Ka86]. The differences in the oxygen-gold chemistry compared with that of silver and copper, particularly the initial resistance of gold to oxidation, and its higher maximum oxidation state, can be attributed

largely to the impact of a relativistic effect (see above). The exceptional low Au-O binding energy can be qualitatively understood on the basis of the HSAB principle [Pe63, Pe68, Pa83, Pe88, Pe93]. The soft gold atom (see Table 2.1 and cf. Ag^+ : 6.96 eV) matches only badly with the hard oxygen (see Table 2.3). A much more favourable combination is that of gold and sulfur (hardness 4.14 eV), as the comparison of the standard formation enthalpies, $\Delta_f H_{298}^0$, of Au_2S_3 (-1116 kJ/mol [Wi63]) and Au_2O_3 (≥ -13 kJ/mol) reveals.

OXYGEN ADSORPTION ON GOLD – Previous work on the adsorption of oxygen on gold surfaces focused on two main problems. First, the question of whether dioxygen is able to chemisorb spontaneously on *clean* gold surfaces at and above room temperature in detectable amounts gave and still gives rise to controversy. The respective references can be found in the article by Saliba et al. [Sa98]. Second, it was widely agreed that a high activation barrier exists for the chemisorption of oxygen on gold. Accordingly, several ways to overcome that activation barrier and to produce chemisorbed oxygen on gold (single)-crystals were investigated. The most important are: (i) dosing of oxygen atoms prepared by thermal dissociation of O_2 [Ca84, Ou86, Sa86] or by a microwave discharge [Li00], (ii) oxygen-ion sputtering [Pi84, Go02a] or exposure to an oxygen plasma [Ro94, Ko01], (iii) dosing of gases which can deposit oxygen atoms like $\text{NO}_2/\text{H}_2\text{O}$ [Wa99] or ozone [Pa90, Ki95, Kr97, Sa98], (iv) electron bombardment or UV irradiation of physisorbed molecular oxygen at low temperatures [Go02], and (v) electrochemical oxidation [Pe84, Tr89, Ki90, Ju00, Ha01, We02].

2.2.2. Carbon monoxide

Carbon monoxide, CO, is isoelectronic with N_2 . The substantial dissociation energy of 1077.10 kJ/mol [Ho85] corresponds to the short bond length of 1.1282 Å and the high molecular vibration frequency of 2143 cm^{-1} . The melting point of CO is 68.1 K, the boiling point 81.7 K. The CO molecule has a remarkably small dipole moment of $\mu = 0.112$ D with the positive end on oxygen (!) [Ho96].

Binary gold carbonyls $\text{Au}_m(\text{CO})_n$ are not stable under normal conditions. $\text{Au}(\text{CO})$ and $\text{Au}(\text{CO})_2$ can be obtained by metal-ligand co-condensation, but they decompose already below 20 K. However, ternary carbonyl gold halogenides, e.g., $\text{Au}(\text{CO})\text{Cl}$, are stable compounds. (This observation may explain why Cl reduces the activity of $\text{Au}/\text{Al}_2\text{O}_3$ catalysts [Oh02].) The increased frequency of the C-O stretching vibration of 2156 cm^{-1} indicates that the contribution of the $\text{Au} \xrightarrow{\pi} \text{CO}$ back donation (see below) is very small in $\text{Au}(\text{CO})\text{Cl}$ [El93]. In concentrated H_2SO_4 , the ions $\text{Au}(\text{CO})^+$ and $\text{Au}(\text{CO})_2^+$ are stable. Both species exhibit high catalytic activity for the carbonylation of olefins [Xu97]. Metastable gold-carbonyl cluster anions, e.g. $\text{Au}_7(\text{CO})_4^-$, were generated in the gas phase [Ny91, Le94, Wa01].

Bonding of CO to metal atoms on surfaces and in carbonyl complexes has been described by a donor-acceptor synergism (Blyholder model [Bl64]). The 5σ orbital, acting as electron donor, and the $2\pi^*$ orbital, as the electron acceptor, interact with the unoccupied and occupied orbitals, respectively, of the metal atom and thereby mediate the interaction between the latter and the C atom of CO. The orbital energies of the metal d levels decrease within a period from left to right and, thereby, also the ability of the metal for back donation. In the case of gold, however, the relativistic destabilization of the 5d levels may counterbalance this effect. Additionally, relativistic stabilization of the 6s and 6p levels should also promote the donor/acceptor synergism. Thus, the CO should form a stronger bond with Au than, e.g., with Ag, which is indeed the case (see Chapter 8).

2.2.3. Carbon dioxide

The linear CO₂ molecule (symmetry $D_{\infty h}$) has a coordinatively saturated C atom and shows much less tendency than CO to form a bond to a metal atom. The C-O bond length of 1.1632 Å is shorter than an ordinary C-O double bond (≈ 1.23 Å), which reflects the fact that the π system extends over the whole molecule. For symmetry reasons, CO₂ possesses no static dipole moment. Under atmospheric pressure, CO₂ sublimates at 194.68 K [Ho85].

2.2.4. Ethylene

Ethylene, C₂H₄, is the simplest alkene and has the symmetry D_{2h} . In contrast to CO, ethylene bonds to metal atoms on surfaces and in numerous complexes [E193] in a *side-on* geometry. The chemical bond can be described by a similar donor/acceptor synergism model as in the case of CO. In this model, first proposed by Dewar [De51] and later extended by Chatt and Duncanson [Ch53], the donating orbital is the HOMO, $1b_{2u}$ (π), and the accepting is the LUMO, $1b_{3g}$ (π^*). Ethylene oxide (oxirane), an important intermediate product in the chemical industry, is produced by catalytical epoxidation of ethylene on a silver catalyst.

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